

Thermodynamic properties of separable square-wave potentials

B. Kollmitzer and P. Hadley*

Institute of Solid State Physics, Graz University of Technology, Graz, Austria

(Dated: January 15, 2013)

Exact analytic solutions to the Schrödinger equation for an electron moving in three dimensional potentials have been studied. These solutions can correspond to metals, semiconductors, or insulators. We show that there is an efficient method to calculate the electron density of states for this class of potentials. From the density of states, the temperature dependence of thermodynamic properties such as the chemical potential and the specific heat were determined. Ten thousand cubic separable potentials were considered. This data makes it possible to identify trends in how the form of the potential is related to the thermodynamic properties of a material.

PACS numbers: 71.20.-b, 65.40.-b

I. INTRODUCTION

To calculate the band structure of a crystal, some initial guess of the electron wave-functions is required. One of the rare cases where analytic solutions to the Schrödinger equation are known for a semiconductor or an insulator are separable potentials that can be written as the sum of three one-dimensional square-wave potentials. Such separable potentials were first considered by Kronig and Penney[1]. There is a simple analytic expression for the energy – wave-number dispersion relation for the well-known problem of an electron moving in a one-dimensional square-wave potential. Here we show that there is also an analytic expression for the density of states for the one-dimensional problem. These results can be simply combined to produce the dispersion relations and density of states of separable three dimensional potentials. A limiting case of this class of potentials is the widely used free electron model which occurs when the amplitude of the square-wave is zero. As the amplitude of the potential increases, the potentials can correspond to metals, semiconductors, or insulators. Normally determining the electronic density of states from the band structure is a computationally intensive process that requires sampling many points of the Brillouin zone. For the separable square-wave potentials, the electronic density of states is however easily calculable as a convolution of three analytically known functions. This makes it easy to calculate the thermodynamic properties corresponding to this class of potentials. From the density of states we can calculate the temperature dependence of thermodynamic quantities such as the chemical potential, the internal energy, the specific heat, the entropy, and the Helmholtz free energy. Half a million plots of the thermodynamic properties of separable potentials are available as online supplementary material[2]. The collective data set allows us to consider how an increase in the amplitude of the potential causes a transition from a metal to an insulator. There are cases where increasing

the amplitude of the potential causes a transition from a metal to an insulator, then back to a metal and then finally back to an insulator.

While band gaps appear in the one-dimensional problem for an arbitrarily small amplitude of the periodic potential, a finite amplitude is needed for the creation of band gaps in three dimensions. In section III we quantify how large the amplitude of the potential must be for bands to be formed for the specific class of three-dimensional potentials we have considered. This minimum amplitude is,

$$V = 0.9 \frac{\pi^2 \hbar^2}{ma^2}. \quad (1)$$

Here V is the amplitude of the potential, \hbar is the reduced Planck's constant, m is the mass of an electron, and a is the lattice constant. The amplitude of the potential necessary for the formation of bands depends strongly on the lattice constant.

II. SOLUTIONS OF THE SCHRÖDINGER EQUATION FOR THE KRONIG-PENNEY POTENTIAL

This section reviews the solutions to the Kronig-Penney model[3, 4] and derives an expression for the one-dimensional density of states which will be used in section III to construct the dispersion relations and densities of states for three-dimensional separable potentials. Figure 1 shows the one-dimensional potential that was first considered by Kronig and Penney[1].

Because of the translational symmetry of the potential, the eigenfunctions of the Hamiltonian are simultaneously eigenfunctions of the translation operator. The eigenfunctions of the translation operator T can be readily constructed from any two linearly independent solutions of the one-dimensional Schrödinger equation. A convenient choice is,

$$\psi_1(0) = 1, \frac{d\psi_1}{dx}(0) = 0, \psi_2(0) = 0, \frac{d\psi_2}{dx}(0) = 1. \quad (2)$$

*Electronic address: p.hadley@tugraz.at

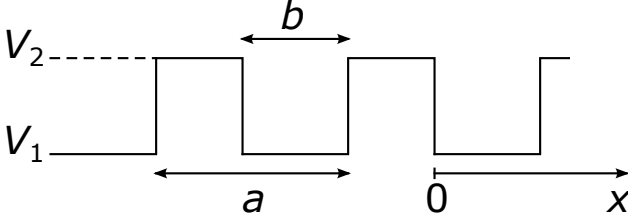


FIG. 1: One-dimensional square-wave potential.

The solutions in region 1 ($0 < x < b$) are,

$$\psi_1(x) = \cos(k_1 x), \psi_2(x) = \frac{\sin(k_1 x)}{k_1}, \quad (3)$$

while the solutions in region 2 ($b < x < a$) are[5],

$$\begin{aligned} \psi_1(x) &= \cos(k_2(x-b)) \cos(k_1 b) \\ &\quad - \frac{k_1}{k_2} \sin(k_2(x-b)) \sin(k_1 b), \end{aligned} \quad (4a)$$

$$\begin{aligned} \psi_2(x) &= \frac{1}{k_1} \cos(k_2(x-b)) \sin(k_1 b) \\ &\quad + \frac{1}{k_2} \sin(k_2(x-b)) \cos(k_1 b). \end{aligned} \quad (4b)$$

Here $k_r = \sqrt{2m(E - V_r)/\hbar^2}$; $r = 1, 2$ is the label of the region, and E is the energy. For energies where k_r is imaginary, the solutions are still real since $\cos(i\theta) = \cosh(\theta)$ and $\sin(i\theta) = i \sinh(\theta)$.

Any other solution can be written as a linear combination of $\psi_1(x)$ and $\psi_2(x)$. In particular, $\psi_1(x+a)$ and $\psi_2(x+a)$ can be written in terms of $\psi_1(x)$ and $\psi_2(x)$. These solutions are related to each other by the matrix representation of the translation operator[6].

$$\begin{bmatrix} \psi_1(x+a) \\ \psi_2(x+a) \end{bmatrix} = \begin{bmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{bmatrix} \begin{bmatrix} \psi_1(x) \\ \psi_2(x) \end{bmatrix}. \quad (5)$$

The elements of the translation matrix can be determined by evaluating Eq. (5) and its derivative at $x = 0$.

$$\begin{bmatrix} \psi_1(x+a) \\ \psi_2(x+a) \end{bmatrix} = \begin{bmatrix} \psi_1(a) & \frac{d\psi_1}{dx}(a) \\ \psi_2(a) & \frac{d\psi_2}{dx}(a) \end{bmatrix} \begin{bmatrix} \psi_1(x) \\ \psi_2(x) \end{bmatrix}. \quad (6)$$

The eigenfunctions and eigenvalues λ of the translation operator are,

$$\begin{aligned} \psi_{\pm}(x) &= \frac{2\psi_2(a)}{\frac{d\psi_2(a)}{dx} - \psi_1(a) \pm \delta} \psi_1(x) + \psi_2(x), \\ \lambda_{\pm} &= \frac{1}{2}(\alpha \pm \delta), \end{aligned} \quad (7)$$

where $\delta = \sqrt{\alpha^2 - 4}$ and

$$\begin{aligned} \alpha &= \psi_1(a) + \frac{d\psi_2(a)}{dx} = 2 \cos(k_2(a-b)) \cos(k_1 b) \\ &\quad - \left(\frac{k_2}{k_1} + \frac{k_1}{k_2} \right) \sin(k_2(a-b)) \sin(k_1 b). \end{aligned} \quad (8)$$

If periodic boundary conditions are used for a potential with N unit cells, then applying the translation operator N times brings the function back to its original position

$$T^N \psi(x) = \psi(x + Na) = \lambda^N \psi(x) = \psi(x). \quad (9)$$

The eigenvalues of the translation operator are therefore the solutions to the equation $\lambda^N = 1$. These solutions are,

$$\lambda_j = \exp\left(\frac{i2\pi j}{N}\right) = \exp\left(\frac{i2\pi a j}{L}\right) = \exp(ik_j a), \quad (10)$$

where j is an integer between $-N/2$ and $N/2$, $L = Na$ is the length of the crystal, and $k_j = 2\pi j/L$ are the allowed k values in the first Brillouin zone. The dispersion relation can be determined by first calculating α for a specific energy and then solving Eqs. (7) and (10) for the wave-number[7],

$$k = \pm \frac{1}{a} \tan^{-1} \left(\frac{\sqrt{4 - \alpha^2}}{\alpha} \right). \quad (11)$$

The dispersion relation can be used to determine the density of states which is needed to calculate the thermodynamic properties of a system of noninteracting electrons[8]. The one-dimensional density of states in k space is $D(k) = 2/\pi$ and thus the density of states in energy is,

$$D(E) = \begin{cases} \frac{2}{\pi} \frac{dk}{dE} = \frac{2}{\pi} \frac{dk}{d\alpha} \frac{d\alpha}{dE} & |\alpha| < 2 \\ 0 & |\alpha| > 2 \end{cases} \quad (12)$$

where

$$\frac{dk}{d\alpha} = \frac{1}{a\sqrt{4 - \alpha^2}},$$

and

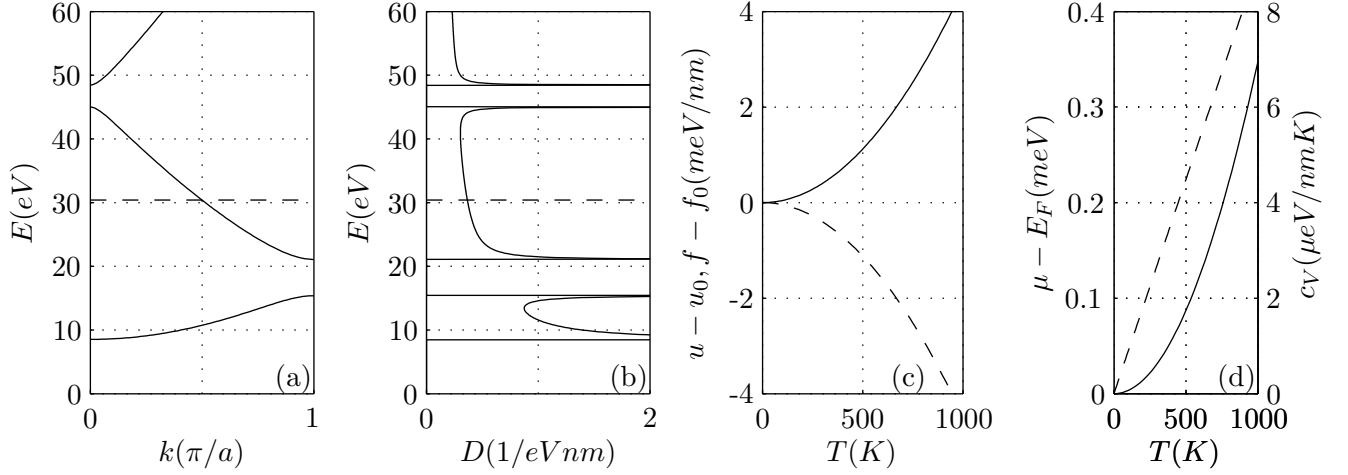


FIG. 2: (a) The energy – wave-number dispersion relation. The dashed line is the Fermi energy. (b) The density of states. (c) The internal energy density (solid line) and Helmholtz free energy density (dashed line). (d) The chemical potential (solid line) and the specific heat (dashed line). All of the plots were drawn for a square-wave potential with the parameters: $V_1 = 0$ eV, $V_2 = 12.5$ eV, $a = 2 \times 10^{-10}$ m, $b = 5 \times 10^{-11}$ m, and an electron density of $n = 3$ electrons/primitive cell.

$$\begin{aligned} \frac{d\alpha}{dE} = & -\frac{m}{\hbar^2} \left(\frac{2b}{k_1} + \left(\frac{k_2}{k_1} + \frac{k_1}{k_2} \right) \frac{(a-b)}{k_2} \right) \cos(k_2(a-b)) \sin(k_1b) - \frac{m}{\hbar^2} \left(2\frac{(a-b)}{k_2} + \left(\frac{k_2}{k_1} + \frac{k_1}{k_2} \right) \frac{b}{k_1} \right) \\ & \times \sin(k_2(a-b)) \cos(k_1b) + \frac{m}{\hbar^2} \left(\left(\frac{k_2}{k_1^2} - \frac{1}{k_2} \right) \frac{1}{k_1} + \left(\frac{k_1}{k_2^2} - \frac{1}{k_1} \right) \frac{1}{k_2} \right) \sin(k_2(a-b)) \sin(k_1b). \end{aligned} \quad (13)$$

Thermodynamic properties such as the chemical potential, the internal energy, the specific heat, the entropy, or the Helmholtz free energy of a system of noninteracting fermions can be calculated from the electron density n , the density of states $D(E)$, and the temperature T .

The chemical potential μ is implicitly defined by the relation,

$$n = \int_{-\infty}^{\infty} D(E) F(E) dE, \quad (14)$$

where $F(E)$ is the Fermi function,

$$F(E) = \frac{1}{\exp\left(\frac{E-\mu}{k_B T}\right) + 1}. \quad (15)$$

Here k_B is Boltzmann's constant. Once the chemical potential has been determined, it can be used to calculate the internal energy density u and the Helmholtz free energy density f .

$$u = \int_{-\infty}^{\infty} E D(E) F(E) dE \quad (16)$$

$$f = \mu n - k_B T \int_{-\infty}^{\infty} D(E) \ln \left(1 + \exp \left(\frac{\mu - E}{k_B T} \right) \right) dE \quad (17)$$

Finally, the specific heat and the entropy are given by the partial derivatives,

$$c_v = \left. \frac{\partial u}{\partial T} \right|_{N,V} \quad \text{and} \quad s = - \left. \frac{\partial f}{\partial T} \right|_{N,V}. \quad (18)$$

The band structure of a one dimensional potential and the corresponding thermodynamic properties are plotted in Fig. 2.

III. THREE-DIMENSIONAL SEPARABLE POTENTIALS

In this section, 5 of the calculated band structures that are available in the supplementary material are presented. This illustrates the variety of results that can be obtained with this simple model. The five examples are a free electron gas, a metal where the charge carriers at the Fermi surface are electron-like, a metal where the charge carriers at the Fermi surface are hole-like, a direct band gap semiconductor, and an indirect band gap semiconductor.

The dispersion relation and density of states for any three-dimensional potential of the form

$$U_{3d}(x, y, z) = U_x(x) + U_y(y) + U_z(z) \quad (19)$$

are easily calculated from the one-dimensional results[9]. The energy of an electron in a three-dimensional separable potential is the sum of the energies of the constituent one-dimensional potentials. The three-dimensional density of states is the convolution of the three one-dimensional densities of states. Once the three-dimensional density of states is known, the thermodynamic quantities can be calculated as outlined above.

The one-dimensional bands can be indexed by integers, 1 corresponding to the band with the lowest energy, 2 to the band with the next lowest energy, etc. The three-dimensional bands can then be indexed by the three integers that correspond to the one-dimensional bands that make up the three-dimensional band. The three dimensional band with the lowest energy is the 111 band. For cubic crystals, the next three bands 211, 121, and 112 are degenerate in energy.

Figure 3 shows the band structure, the density of states, and corresponding thermodynamic properties for a constant potential that corresponds to a free electron gas. The band structure in Fig. 3a is plotted along a path in the Brillouin zone going from the M point (0.5, 0.5, 0) through the points Γ (0, 0, 0), X(0.5, 0, 0), M, R (0.5, 0.5, 0.5), X, Γ , ending at the point R. All of the standard results for a free electron gas are reproduced by the numerical calculation. The dispersion relation is parabolic; the density of states increases with the square root of the energy and the specific heat is a linear function of the temperature.

Figures 4 and 5 show the results for a potential with an amplitude of 4.2 eV, $a = 0.2$ nm, and $b = 0.09$ nm. Gaps open in the dispersion relation at the Brillouin zone boundaries and some kinks appear in the density of states. These kinks make both the analytical and numerical evaluation of the thermodynamic properties difficult. Both Figs. 4 and 5 correspond to metals but in Fig. 4 the electron density is 2 electrons/primitive cell and the density of states is increasing at the Fermi energy while in Fig. 5 the electron density is 1 electron/unit cell and the density of states is decreasing at the Fermi energy. The material in Fig. 4 has a Fermi surface that consists of electron-like states and the chemical potential decreases with increasing temperature as it does for the free electron gas of Fig. 3. The material in Fig. 5 has a Fermi surface that consists of hole-like states and consequently the chemical potential increases with increasing temperature.

Figure 6 shows the band structure for a material with two band gaps. The lower band gap is indirect with a band gap energy of 3.9 eV. The upper band is direct with a band gap energy of 0.4 eV. If the material shown in Fig. 6 had 2 electrons/primitive cell, the lowest band would be completely filled and it would be an insulator. For an electron density of 8 electrons/primitive cell, the

Fermi energy lies in the second band gap (illustrated by the dashed line in Fig. 6a). The thermodynamic properties in Figs. 6c and 6d were calculated assuming an electron density of 8 electrons/primitive cell. Since this material is a semiconductor, the electronic contribution to the specific heat is negligible at low temperature and increases exponentially at high temperatures. The chemical potential of a semiconductor is a linear function of the temperature.

Figure 7 shows the band structure for a potential where the 311 band has moved down lower than the 221 band. In this case the lower band is indirect with a band gap of 4.7 eV and the upper band gap is also indirect with a band gap energy of 0.5 eV. For an electron density of 8 electrons/primitive cell, the Fermi energy lies in the second band gap where the dashed line is drawn and the material is an indirect band gap semiconductor.

The dispersion relations, densities of states, and thermodynamic properties like those shown in Fig. 3-7 were calculated for 10000 cubic potentials. For these calculations, it is convenient to normalize the Schrödinger equation so that length is measured in terms of the lattice constant a . When this is done, energies are measured in units of $\pi^2 \hbar^2 / 2ma^2$ and there are only two independent parameters in the problem, which can be taken to be $\tilde{b} = b/a$ and $\tilde{V} = 2ma^2V/\pi^2 \hbar^2$. Here $V = V_2 - V_1$. The calculations were performed for normalized parameters in the range $\tilde{b} = (0, 1)$ and $\tilde{V} = (0, 27)$. It becomes more difficult to perform the numerical calculations of the thermodynamic properties for large values of \tilde{V} . The upper limit of $\tilde{V} = 27$ corresponds to the amplitude where our calculations of the thermodynamic properties become unreliable.

Figure 8 shows the sizes of the first two band gaps that occur. The three-dimensional potential must have a finite amplitude for there to be a band gap.

IV. THERMODYNAMIC PROPERTIES OF THE METALS

The band structures of the potentials that were studied always correspond to metals when there is no band gap. This region includes the free electron model at $\tilde{V} = 0$ as well as δ -function potentials in the regions near $\tilde{b} = 0$ and $\tilde{b} = 1$. When band gaps occur, the situation is more complicated. The potentials can correspond to metals, semiconductors, or insulators depending on the electron density. We compared the thermodynamic properties of these metals to results obtained by using the Sommerfeld expansion. Sommerfeld showed that the electronic contribution to the thermodynamic properties of metals can be approximated in terms of just two quantities: the density of states at the Fermi energy $D(E_F)$ and the derivative of the density of states at the Fermi energy[10]

$$D'(E_F) = \left. \frac{dD(E)}{dE} \right|_{E_F}. \quad (20)$$

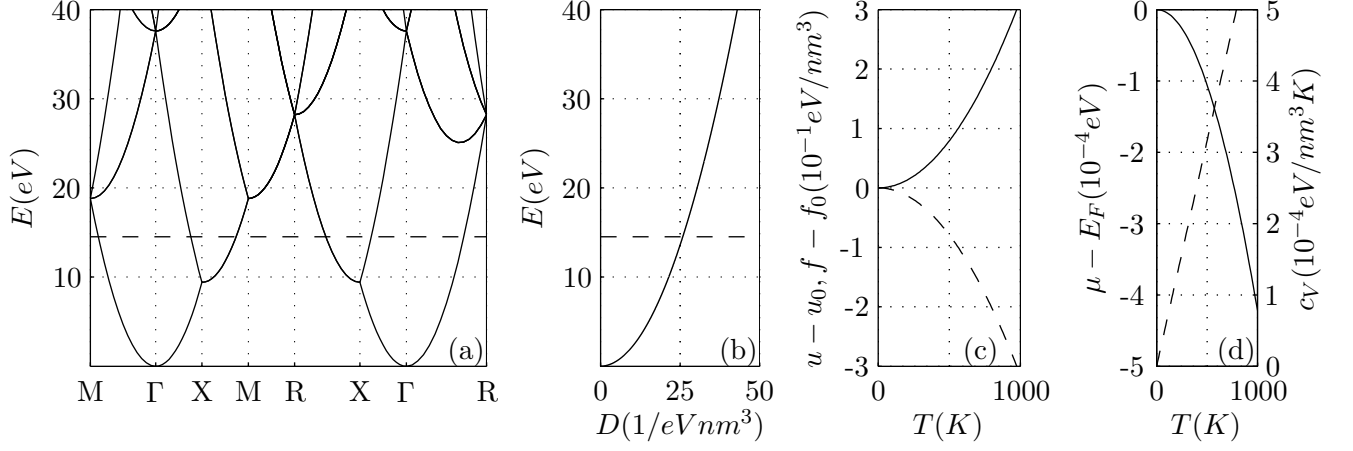


FIG. 3: The band structure and thermodynamic properties of a free electron gas. (a) The energy-momentum dispersion relation. The dashed line is the Fermi energy. (b) The density of states. (c) The internal energy density (solid line) and the Helmholtz free energy density (dashed line). (d) The chemical potential (solid line) and the specific heat (dashed line). All plots are for a cubic potential with the parameters: $V_1 = 0$ eV, $V_2 = 0$ eV, $a = 0.2$ nm, $b = 0.09$ nm, and an electron density of $n = 2$ electrons/primitive cell.

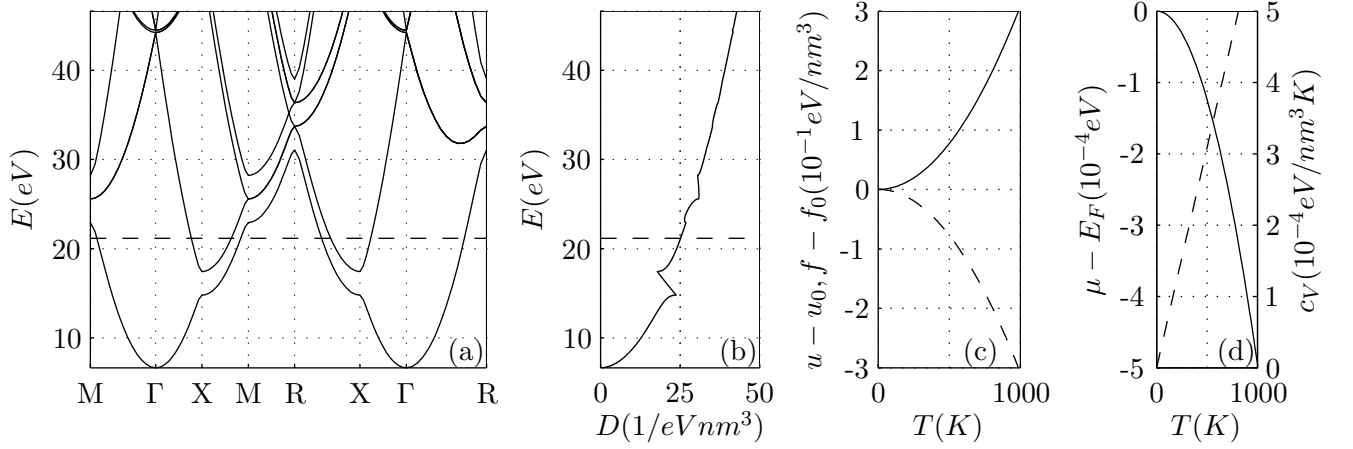


FIG. 4: The band structure and thermodynamic properties for a cubic potential $V_1 = 0$ eV, $V_2 = 4.2$ eV, $a = 0.2$ nm, $b = 0.09$ nm and $n = 2$ electrons/primitive cell. (a)-(d) as in Fig. 3.

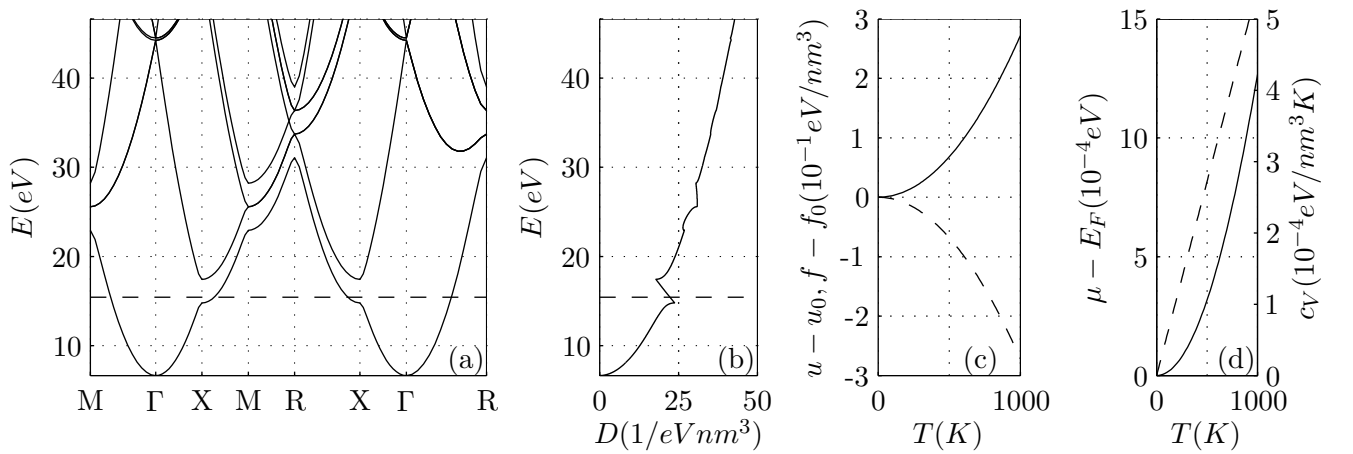


FIG. 5: The band structure and thermodynamic properties for a cubic potential $V_1 = 0$ eV, $V_2 = 4.2$ eV, $a = 0.2$ nm, $b = 0.09$ nm and $n = 1$ electrons/primitive cell. (a)-(d) as in Fig. 3.

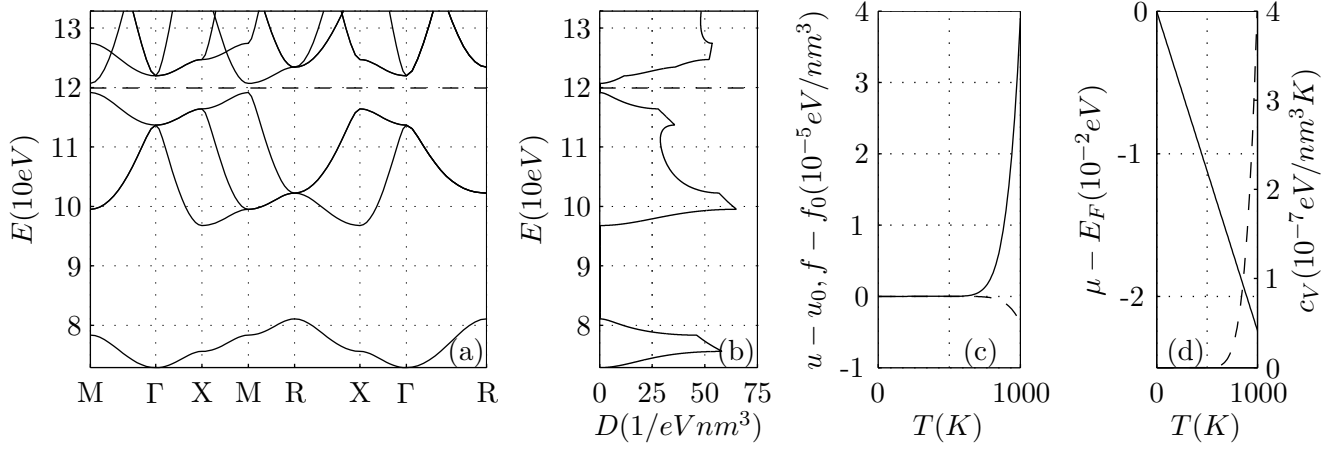


FIG. 6: The band structure and thermodynamic properties for a cubic potential $V_1 = 0\text{ eV}$, $V_2 = 8.8\text{ eV}$, $a = 0.4\text{ nm}$, $b = 0.21\text{ nm}$ and $n = 8$ electrons/primitive cell. This band structure corresponds to a direct band gap semiconductor. (a)-(d) as in Fig. 3.

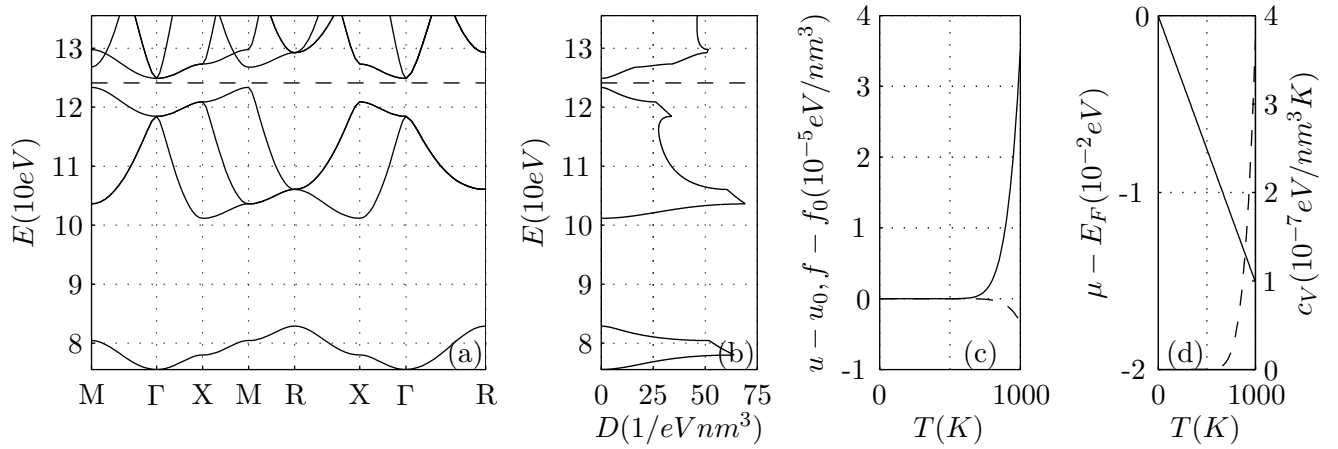


FIG. 7: The band structure and thermodynamic properties for a cubic potential $V_1 = 0\text{ eV}$, $V_2 = 9.5\text{ eV}$, $a = 0.4\text{ nm}$, $b = 0.19\text{ nm}$ and $n = 8$ electrons/primitive cell. This band structure corresponds to an indirect band gap semiconductor. (a)-(d) as in Fig. 3.

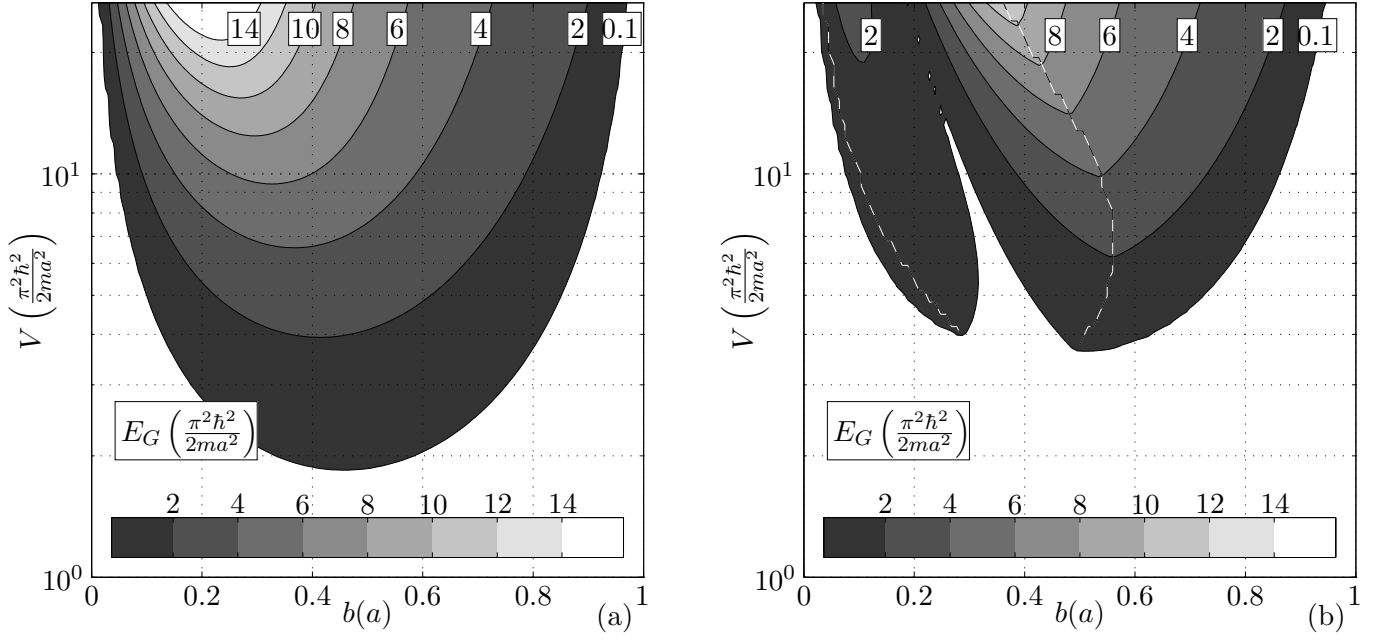


FIG. 8: (a) The band gap of the lowest gap between band 111 and the degenerate bands 112, 121, and 211 in units of $\pi^2 \hbar^2 / 2ma^2$. This band gap is always indirect. (b) The second band gap. The dashed lines in (b) indicate the transitions from direct to indirect band gaps. The indirect band gaps are in between the two dashed lines. Note that there is a reentrant regime at $b = 0.3$ where an increase in the amplitude V causes a transition from metal to insulator, then back to a metal and finally to an insulator.

To lowest order in the temperature T , the Sommerfeld expression for the chemical potential, the internal energy, specific heat, entropy, and Helmholtz free energy are,

$$\mu \approx E_F - \frac{\pi^2}{6} (k_B T)^2 \frac{D'(E_F)}{D(E_F)}, \quad (21)$$

$$u \approx u(T=0) + \frac{\pi^2 D(E_F)}{6} (k_B T)^2, \quad (22)$$

$$c_v \approx \frac{\pi^2 D(E_F)}{3} k_B^2 T, \quad (23)$$

$$s \approx \frac{\pi^2 D(E_F)}{3} k_B^2 T, \quad (24)$$

$$f \approx u(T=0) - \frac{\pi^2 D(E_F)}{6} (k_B T)^2. \quad (25)$$

Figure 9 shows the value of the density of states at the Fermi energy and its derivative for an electron density of $n = 1$ electron/primitive cell. This figure makes it possible to estimate the thermodynamic properties of the metals by substituting the values for $D(E_F)$ and $D'(E_F)$ into Eqs. (21)–(25).

The Sommerfeld expansion assumes that the density of states is a smoothly varying function in an energy range about $k_B T$ wide in the vicinity of the Fermi energy. However, the density of states must contain kinks known as

Van Hove singularities[11]. If the Fermi energy is within an energy $k_B T$ of one of the kinks, then the assumptions of the Sommerfeld theory are invalid. The numerical simulations in the supplementary material show that the Sommerfeld approximation is valid in the majority of cases where there are no band gaps. When gaps are present, the bands are narrow and it is more likely that the Sommerfeld theory fails. In the case of extremely narrow bands it becomes difficult to determine the temperature dependence of the thermodynamic properties reliably because of the discontinuities in the density of states.

V. THERMODYNAMIC PROPERTIES OF THE SEMICONDUCTORS AND INSULATORS

If the Fermi energy falls in a band gap so that the material is a semiconductor or an insulator, the density of states at the Fermi energy and its derivative are not suitable for describing the thermodynamic quantities. Instead, it is common to specify the band gap and the effective masses of the electrons and holes.

For cubic crystals, the first gap appears above the 111 band and beneath the next three bands (211, 121, and 112) which are degenerate due to symmetry reasons. Above these three degenerate bands, a second energy gap sometimes appears. The Fermi energy lies in the first gap for an electron density of 2 electrons per unit cell and it can only be in the second gap for an electron density of

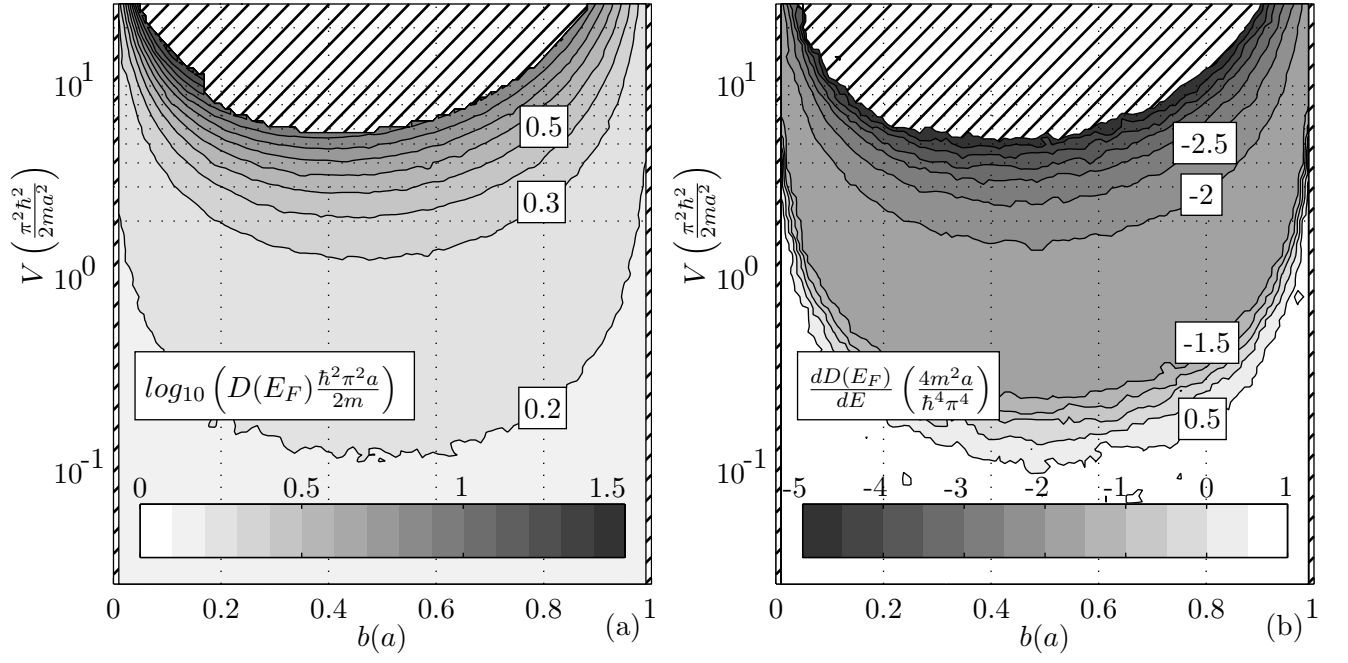


FIG. 9: The density of states at the Fermi energy and the derivative of the density of states at the Fermi energy for an electron density of $n = 1$ electrons/primitive cell. It was not possible to determine the density of states at the Fermi energy reliably in the crosshatched regions. Similar plots for electron densities 2–10 electrons/primitive cell are available in the supplementary information online.

8 electrons per unit cell.

The first gap is always indirect with the maximum of the valence band occurring at R. The minimum in the conduction band for the first gap occurs at X. The second band is sometimes direct and sometimes indirect. The valence band maximum of the second gap is always at M. When the second band gap is direct, the conduction band minimum is also at M (see Fig. 6) but when the second band gap is indirect, the conduction band minimum is at Γ (see Fig. 7).

The effective masses near the top of the valence band and bottom of the conduction band can be found by linearizing α given by Eq. (8) near the band edges and inserting this into Eq. (11). The effective masses of electrons and holes are,

$$m_e^* = \frac{\hbar^2}{2a^2} \left(-\frac{d\alpha}{dE} \Big|_{E=E_c} \right) \text{ and} \quad (26a)$$

$$m_h^* = \frac{\hbar^2}{2a^2} \left(\frac{d\alpha}{dE} \Big|_{E=E_v} \right). \quad (26b)$$

Here E_c is the energy at the bottom of the conduction band and E_v is the energy at the top of the valence band. The effective masses are plotted in Fig. 10.

The thermodynamic properties of semiconductors or insulators are typically calculated using the Boltzmann approximation. In this approximation, the density of

states near the Fermi energy is described by the function,

$$D(E) = \begin{cases} (2m_h^*)^{3/2} \frac{\sqrt{E_v - E}}{2\pi^2 \hbar^3} & E < E_v \\ 0 & E_v < E < E_c \\ (2m_e^*)^{3/2} \frac{\sqrt{E - E_c}}{2\pi^2 \hbar^3} & E_c < E \end{cases} \quad (27)$$

In the Boltzmann approximation it is further assumed that in the conduction band the Fermi function in Eqs. (14),(16)–(18) can be replaced by a Boltzmann factor $F(E) \approx \exp((\mu - E)/k_B T)$ while in the valence band $F(E) \approx 1 - \exp((E - \mu)/k_B T)$. The result for the chemical potential of a semiconductor in this approximation is found in many textbooks[12, 13]. The chemical potential of a semiconductor or insulator is a linear function of the temperature.

$$\mu \approx \frac{E_v + E_c}{2} - \frac{3}{4} k_B T \ln \left(\frac{m_e^*}{m_h^*} \right) \quad (28)$$

The Boltzmann approximation can also be used to calculate the electronic contribution to other thermodynamic quantities in terms of the band gap and the effective masses.

$$u \approx u(T=0) + \frac{\sqrt{2\pi}}{2\pi^2 \hbar^3} (m_e^* m_h^*)^{3/4} \exp \left(\frac{-E_g}{2k_B T} \right) \times (k_B T)^{3/2} (3k_B T + E_g), \quad (29)$$

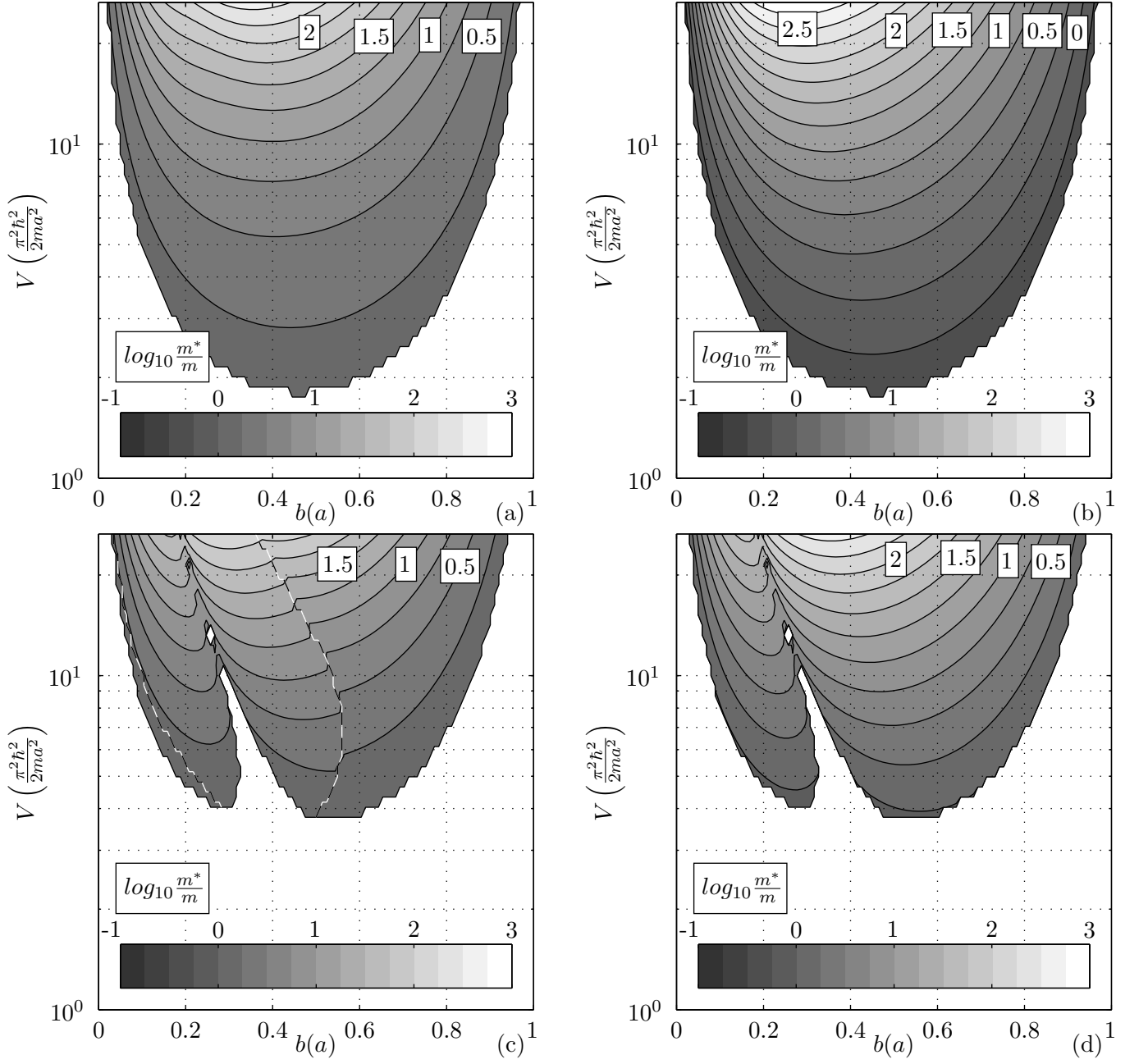


FIG. 10: (a) Effective masses of electrons in the first band gap. (b) Effective masses of holes in the first band gap. (c) The effective masses of electron in the second band gap. The dashed lines indicate the transitions from direct to indirect band gaps. The indirect band gaps are in between the two dashed lines. (d) The effective masses of holes in the second band gap.

$$c_v \approx \frac{\sqrt{2\pi}}{2\pi^2 \hbar^3} (m_e^* m_h^*)^{3/4} \exp\left(\frac{-E_g}{2k_B T}\right) (k_B T)^{3/2} \times \left(\frac{15}{2} k_B + \frac{3E_g}{T} + \frac{E_g^2}{2k_B T^2}\right), \quad (30)$$

$$s \approx \frac{\sqrt{2\pi}}{2\pi^2 \hbar^3} (m_e^* m_h^*)^{3/4} \exp\left(\frac{-E_g}{2k_B T}\right) (k_B T)^{3/2} \times \left(5k_B + \frac{E_g}{T}\right), \quad (31)$$

$$f \approx u(T=0) - \frac{\sqrt{2\pi}}{\pi^2 \hbar^3} (m_e^* m_h^*)^{3/4} (k_B T)^{5/2} \times \exp\left(\frac{-E_g}{2k_B T}\right). \quad (32)$$

Here E_g is the band gap. The Boltzmann approximation assumes that there are no other kinks in the density of states besides the square root behavior described by Eq. (27) within $k_B T$ of the band edge. This approximation works best for small band gaps. For large band gaps the bands are narrow and there are Van Hove singularities near the band edges. The electronic contributions to the thermodynamic quantities of semiconductors and insulators are exponentially suppressed at low temperatures by the factor $\exp(-E_g/2k_B T)$ and are often simply ignored. Equations (29)–(32) can be used to estimate the temperatures where it is no longer reasonable to ignore the electronic contribution to the thermodynamic properties of semiconductors.

VI. CONCLUSIONS

The classic problem of electrons moving in a 1-D square-wave potential was considered and expressions were derived for the density of states and the effective masses of electrons and holes. These expressions allowed us to efficiently calculate the band structure and electronic contribution to the thermodynamic properties in

3-D separable square-wave potentials. This relatively simple model produces a wide range of band structures including metals, semiconductors, and insulators. Plots were presented showing the parameters for which band gaps appear. It was observed that for this class of potentials, band gaps only appear when $V > 0.9\pi^2\hbar^2/ma^2$. Thus the condition for the existence of band gaps depends strongly on the lattice constant. The density of states at the Fermi energy and its derivative as well as the effective masses of the electrons and holes were also calculated. This makes it possible to estimate the thermodynamic properties using the standard approximations of the Sommerfeld expansion for metals and the Boltzmann approximation for semiconductors. Expressions were derived for the thermodynamic properties of semiconductors in the Boltzmann approximation. These simple models assume that the density of states is a smooth function in an energy range $k_B T$ wide. For those cases where a Van Hove singularity causes the density of states not to be a smooth function, the thermodynamic properties were calculated numerically and the results are available in the supplementary material.

-
- [1] R. de L Kronig and W. G. Penney, Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences **130**, 499 (1931).
 - [2] *Supplementary material*, <http://lamp.tu-graz.ac.at/~hadley/ss1/separablecrystals/index.html>.
 - [3] D. McQuarrie, The Chemical Educator **1**, 1 (1996).
 - [4] F. Szmulowicz, European Journal of Physics **18**, 392 (1997).
 - [5] E. Merzbacher, *Quantum Mechanics* (Wiley, New York, NY, 1961).
 - [6] W. Magnus and S. Winkler, *Hill's Equation* (Dover Publications, New York, NY, 1966), 1st ed.
 - [7] C. M. Bender, G. V. Dunne, and P. N. Meisinger, Physics Letters A **252**, 272 (1999), ISSN 0375-9601.
 - [8] Y. Lin and M. S. Dresselhaus, Phys. Rev. B **68**, 075304 (2003).
 - [9] A. Berezin, Phys. Rev. B **33**, 2122 (1986).
 - [10] A. Sommerfeld, Zeitschrift für Physik A Hadrons and Nuclei **47**, 1 (1928).
 - [11] J. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, Cambridge [England], 1964).
 - [12] C. Kittel, *Introduction to solid state physics* (Wiley, Hoboken NJ, 2005), 8th ed.
 - [13] N. Ashcroft, *Solid state physics* (Brooks/Cole, [South Melbourne], 1976).